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HEAT-STERILIZABLE, REMOTELY ACTIVATED BATTERY DEVELOPMENT PROGRAM

PHASE I

First Quarterly Report

Period: July 1 to September 30, 1968

Contract No. 952214
NAS 7-100

October 25, 1968

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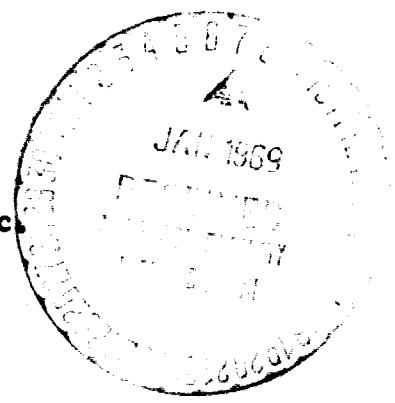

ELECTRONICS DIVISION
Eagle-Picher Industries, Inc.
Couples Department
Joplin, Missouri

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"This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, as sponsored by the National Aeronautics and Space Administration under Contract NAS 7-100."

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ABSTRACT

This report initiates the quarterly progress reporting for development of a heat sterilizable, sealed, remotely activated battery per Contract No. 952214 between Jet Propulsion Laboratory and Eagle-Picher Industries, Inc. The work effort is proceeding in Phase I defined by contract as an investigation of basic cell and battery components and materials to characterize individual capabilities to withstand the heat sterilization routine and retain desirable properties.

Testing of absorbent type plate separation materials of common variety revealed that cellulosics, asbestos and pure nylon were least affected by the dry sterilization routine. Polypropylene types of separation material were physically changed causing structure breakdown.

Preliminary results indicate that sterilization does not appreciably alter the wetting and retention characteristics of the surviving materials.

A preliminary survey of possible propellants which would be capable of heat sterilization without degradation of properties has been conducted. The result of this survey was that three types of propellants may be applicable. These include magnesium-viton perchlorate, ammonium picrate, and ammonium perchlorate formulations. Other propellants may be investigated where applicable.

One informal test was conducted with a reverse bend electrolyte reservoir. The reservoir was heat sterilized with no degrading effects ascertained.

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1.0 INTRODUCTION

This report presents the results of investigating efforts during the first quarter ending 30 September 1968. The presentation includes discussion of the planned direction of effort in the elementary investigation of basic cell and battery materials. This effort, termed Phase I, would necessarily result in a basis for selection of optimum material and/or material combinations for the fabrication of a prototype battery assembly.

Phase I is arranged to begin evaluation of cell materials and pyrotechnic devices as a prerequisite to detailed evaluation of battery assembly items and the electrolyte reservoir.

Review of available reports related to battery sterilization has been conducted in an effort to gain an appreciation for problem areas and methods of solution. The majority of prior battery (sterilization) developments has been in the area of the sterilization of wet, uncharged electrode, secondary cells. Many of the problems encountered in secondary battery development would not be expected to significantly affect the performance of a short life, primary cell. The sterilization of dry, charged electrodes does significantly affect the composition to a point where efficiency is sacrificed. Information associated with the dry sterilization of the charged cell and components is required to proceed with the development. This initiating effort is coupled with evaluation of components and materials necessary for remote activation.

2.0 TECHNICAL DISCUSSION

2.1 Cell Electrodes

A standard sized, die cut plate configuration has been selected for evaluation with expanded silver grid and an active material area of 3.25 In^2. Both formed and pasted silver oxide and zinc plates are to be evaluated for effects of heat sterilization. Effort will be directed toward determination of changes in material composition and/or structure with particular attention to those electrode characteristics which significantly affect performance efficiency.

2.1 Cell Electrodes (Continued)

Conclusive evidence is available regarding the decomposition of divalent silver oxide to monovalent silver oxide and silver when exposed to excessive temperature. The time-temperature routine of heat sterilization causes a rapid decomposition to the more stable monovalent silver oxide with an energy capability of approximately 40% less than that originally formed into the plate.

Preliminary tests have shown that silver-oxide plate change can occur in two different modes. The first mode observed was the reduction of the electrode surface to silver with internal layer(s) of divalent silver and/or monovalent silver. The second mode was observed as an apparent homogeneous reduction to monovalent silver oxide without the obvious surface condition of the first mode. The exact explanation of this occurrence was not attained in this test, however, it may well be attributed to recombination of available oxygen or electrode apparent density. In any case, the condition warrants further attention during subsequent testing.

2.2 Plate Separation

Testing has been accomplished upon several types of absorbent separator materials in an effort to determine characteristics and screen the different types for continued testing. The criteria for acceptance of these tests was simply whether the material would withstand heat sterilization without physically disintegrating. The screening procedure involved measurements of sample length, width and weight. Length and width were measured to the nearest 1/64th of an inch and weight to the nearest 0.1 milligram. Efforts to measure thickness were not considered to be accurate for reporting purposes. Changes in thickness are noted as relative observations.

Six (6) samples of each type were cut to approximately 2" x 5" for evaluation. Two (2) samples each were selected for the first screening sterilization. Subsequent to obtaining the physical measurements, the samples were suspended in an oven maintained at 135°C for a period of 120 hours.

2.2 Plate Separation (Continued)

The following general categories of materials were subjected to the sterilization cycle:

A) Asbestos (Items 1 - 10)

B) Nylon (Items 11 & 12)

C) Nylon/Binder (Items 13 - 19)

D) Nylon/Polypropylene (Item 20)

E) Polypropylene (Item 21)

F) Polypropylene/Binder (Item 22)

G) Cellulosics (Items 23 - 25)

Twenty-five (25) physically different materials were involved. In general, the categories least affected by sterilization were pure nylon (B), cellulosics (G), and asbestos (A). Categories severely affected were polypropylene types (D, E, and F).

The following Table I, presents the results of the cycle in terms of actual materials used and measurements results. The following discussion is presented concerning each material category. None of the samples were pretreated in any manner except Items 1 and 2, Table I. These samples of asbestos board were heat treated prior to the sterilization cycle to remove remaining binder material.

Asbestos board and cloth were tested supplied by Johns-Manville and Raybestos-Manhattan, respectively. Dimensional and appearance changes of all types tested were insignificant except the glass-filled asbestos (7410, Items 5 & 6) displayed a significant thickness change. The asbestos board (Items 1 - 4) increased in weight following sterilization. Possible moisture pickup may account for this, however, precautions were taken to avoid moisture

TABLE I

PHYSICAL CHANGES TO SEPARATION MATERIAL FOLLOWING HEAT STERILIZATION

Item No.	Material Type	Description	Supplier	Average (±.5%) Dimensional Change (%)		Average (±.01%) Weight Change %	Remarks
				Width	Length		
1	Asbestos	.010 Sintered	Johns-Manville	-.01	+.12	+.58	No Change
2	Asbestos	.020 Sintered	Johns-Manville	-.32	-.02	+.42	" "
3	Asbestos	.010 As Rec'd	Johns-Manville	+.15	-.04	+.39	" "
4	Asbestos	.020 As Rec'd	Johns-Manville	+.25	-.12	+.10	" "
5	Asbestos	7410 40% Glass	Raybestos	-.18	+.18	-1.69	" "
6	Asbestos	7410/5 40% Glass	Raybestos	-.05	+.29	-1.33	" "
7	Asbestos	7401 5% Binder	Raybestos	-.12	+.33	-1.80	" "
8	Asbestos	7401/5 5% Binder	Raybestos	-.35	+.06	-2.66	" "
9	Asbestos	7301 Sintered	Raybestos	-.12	-.07	-1.04	" "
10	Asbestos	7301/5 Sintered	Raybestos	-.12	-.08	-.08	" "
11	Nylon (100%)	Non-Woven KS-900	Kimberly-Stevens	+.12	+.75	-1.56	Slight Yellowing
12	Nylon (100%)	Woven 9031	Stern & Stern	-.41	-.51	+.02	Slight Yellowing
13	Nylon/ Dynel	75/25 M1406	Kendall Mills	-1.72	-1.61	-2.10	Brown
14	Nylon/B	2504K	Pellon Corp.	-1.87	-4.12	-6.10	Dark
15	Nylon/B	2505	Pellon Corp.	-3.18	-1.39	-2.90	Yellow
16	Nylon/B	2505K	Pellon Corp.	-1.25	-2.49	-2.98	Yellow, Distorted
17	Nylon/B	2505ML	Pellon Corp.	-5.57	-2.32	-8.77	Dark Yellow, Distorted, Separated
18	Nylon/B	2506K	Pellon Corp.	-3.99	-2.94	-9.63	Yellow, Brittle
19	Nylon/B	2506ML	Pellon Corp.	-1.50	-3.77	-7.05	Yellow, Distorted
20	Nylon/PP	SM124.3	Kendall Mills	-28.48	-14.78	-9.00	Yellow, Distorted, Swelled
21	Polypro-pylene	EM476	Kendall Mills	---	---	---	Disintegrated
22	Polypro-pylene	2530	Pellon Corp.	---	---	---	Disintegrated
23	Rayon	R75D	Chicopee Mills	-2.24	-1.09	+1.81	Lt. Yellow Distorted
24	Cotton	2409	Kendall Mills	+.05	-.64	-2.64	Slight Discoloration
25	Hemp	Filpaco 4366T	Dexter	-.44	-.60	-1.37	Slight Discoloration

2.2 Plate Separation (Continued)

inclusion and the asbestos cloth (Items 5 - 10) lost weight. Sintering the asbestos board does indicate that the weight increase was due to moisture. The weight loss in the asbestos cloth is due primarily to the 5% organic binder utilized. The pyrolyzed material (Items 9 & 10) suffered the least weight loss of the asbestos cloth group indicating that the pretreatment removed significant amounts of binder.

Woven nylon (100%, Item 12) was selected to demonstrate the capabilities of nylon separation in its purest form. A non-woven type (Item 11) was also tested which is specified to be 100% nylon. The woven type nylon displayed very slight weight change relative to all other samples tested. Dimensional changes were insignificant. The non-woven type (KS900, Item 11), lost approximately 1.5% of its weight indicating possible presence of binding material.

The nylon/binder group of non-woven materials (Items 13 - 19) in each case demonstrated significant change dimensionally and in appearance. The varying degree of change observed is attributed to the percentage binder material utilized in each specific material. Information on the exact composition of the Pellon materials was not immediately available.

The polypropylene materials (Items 20 - 22) were severely affected by the sterilization routine. Polypropylene and polypropylene with binder were reduced essentially to a powder during the cycle. Subsequent measurement of these samples was not possible. The nylon/polypropylene material (Item 20) suffered severe shrinkage and distortion but was relatively intact for measurements. It appears obvious that the 50% polypropylene contributed extensively to the degradation of Item 20.

Examples of natural and synthetic organic cellulosic fibers were subjected to the sterilization routine with relative success. The synthetic rayon with cellulosic binder (Item 23) suffered a slight distortion and discoloration. An increase in weight was noted.

2.2 Plate Separation (Continued)

Both the cotton and hemp fiber types (Items 24 and 25) appeared to survive the routine with only slight discoloration, insignificant dimensional changes and weight loss most probably attributed to moisture. The cotton material is pre-pressed to thickness prior to normal usage and expanded to approximately its original thickness during sterilization.

All of the materials tested in this series have been previously utilized in various battery applications. Cotton, hemp and asbestos have been used as the sole separation material in high-rate, short life, remotely activated batteries. With the exception of asbestos, none of these materials are particularly well known for their high temperature stability characteristics. It is concluded, however, that both nylon and cellulosics are capable of withstanding the sterilization routine without appreciable physical change. Dry sterilization of polypropylene apparently destroys the material structure. This condition was also observed earlier subsequent to performing a sterilization cycle on a molded polypropylene cell case.

The usage of additional materials as a binding system will cause separation degradation unless the binder is compatible with the parent material. Preferably, in this application, the separation system would be limited to the acceptable parent material without binder or additional strengthening additives. Based upon the results of this investigation, the more favorable materials for a heat sterilizable separation are asbestos, pure nylon and natural cellulosic fibers. Additional tests are to be accomplished on these materials for verification of results. Also, other materials will be investigated as they become available. Tests are beginning upon surviving materials to determine their relative wetting and electrolyte retention capabilities.

Preliminary results have indicated that the sterilization routine does not significantly affect the electrolyte absorption and retention characteristics of the tested separation materials.

2.3 Electrolyte Solution

The electrolyte reservoir presently utilized in remotely activated batteries will adequately retain the solution at sterilization temperatures in any concentration. This will allow freedom to investigate various concentrations relative to electrical performance and corrosive effects. These are to be initiated using 30% by weight potassium hydroxide with efforts directed toward limiting solution contamination and attaining optimum electrical performance.

2.4 Cell Case/Sealing

Basic materials will be studied to determine the effects of dry sterilization upon important mechanical and physical properties. Review of manufacturer information and previous effort in this area has shown that polyphenylene oxide has the best combination of properties in the field of common thermoplastics. Polysulphone has excellent properties and is relatively transparent. In the field of thermoplastics, the following basic forms are under consideration:

1) Polyphenylene Oxide
2) Polysulfone
3) Fluorocarbons
4) Polyimides
5) Polycarbonate
6) Acetals
7) Chlorinated Polyethers

Controlling the acceptability of the case material in addition to thermal stability would be the ability to easily form the material and effect a reliable seal. Various methods of sealing will be evaluated with all materials determined feasible for usage.

2.5 Battery Container

Two types of metals presently used in Eagle-Picher Battery containers shall be considered for this application. Each offers some advantages along with some recognizable penalties.

The most common material is stainless steel. This material offers excellent retention of properties throughout the required temperature range. Since stainless steel has a relatively high tensile

2.5 Battery Container (Continued)

strength, lighter gages may be used allowing the metal to be easily formed. The material weight is the main disadvantage of stainless steel.

Titanium is the second material under consideration. This material offers both excellent strength and weight savings. In comparison to stainless steel, titanium is not as economical to fabricate but may be reliably formed. Titanium offers a weight savings of approximately 40% over stainless steel.

Although the primary effort shall be directed toward the study of these two (2) metals, some of the polymers studied in cell case construction may be found to be capable of being utilized as the container.

Container designs presently available at Eagle-Picher shall be utilized for study. Measurements shall be made of any distortion occurring due to heat sterilization. This study shall be conducted later in the program.

2.6 Electrolyte Reservoir and Pyrotechnics

This study shall be divided into two (2) parallel programs. Each shall be analyzed separately with the compatibility of the two demonstrated in the final analysis.

The primary effort on the reservoir shall be directed toward configurations utilized in Eagle-Picher remote activated batteries. The effects of heat sterilization on the reservoir shall be determined with measurements made as to the distortion (i.e., contraction, expansion) of the assembly. The effects of the expansion of electrolyte and air during sterilization on the diaphragms shall be determined.

An informal test was performed on a slight reverse bend electrolyte reservoir. The reservoir was filled to approximately 90% of capacity with 1300 KOH and was sealed by two (2) frangible copper diaphragms, .0025 inch thick at each end. When placed in a 135°C ambient, the reservoir successfully contained the internal pressure from the expansion of electrolyte and air. No

2.6 Electrolyte Reservoir and Pyrotechnics (Continued)

external electrolyte crystals or liquid were detected. The reservoir had not distorted enough to visually detect any deformation. The primary purpose for this test was not to determine distortion of the reservoir but to ascertain its capabilities to withstand the thermal expansion of the liquid and gas.

Two reservoirs are being fabricated for testing. The first is the standard wrap around tubular reservoir. A second reservoir is a reverse bend reservoir comprised of a series of lengths of parallel copper tubing joined with 180° reverse bends. These reservoirs shall be filled with electrolyte, analyzed dimensionally, sterilized, measured again while hot, cooled and measured again. Weights shall be determined before and after sterilization. The diaphragms shall be examined for excessive distortion or leakage due to internal expansion.

In studying the pyrotechnics to be used with the reservoir, emphasis shall be placed on the compatibility of the pressure-time relationship of gas generator. Once a propellant is obtained generators shall be constructed and tested in a closed bomb. Measurements shall be made as to pressure versus time and volume of gas generated.

As a result of a preliminary survey of the propellant manufacturers, four (4) manufacturers have responded. Each manufacturer was asked to recommend his own particular propellant. Those recommended included magnesium viton perchlorate (Atlantic Research), ammonium picrate (Space Ordnance Systems), and ammonium perchlorate (Atlas Chemical Industries and Talley-Industries).

The magnesium viton perchlorate has no history of use in this application. According to the manufacturer, a special formulation would be required to retard the burning rate to that required. With an auto-ignition point in excess of 600°F, no degradation would be expected at or below 135°C.

2.6 Electrolyte Reservoir and Pyrotechnics (Continued)

Space Ordnance Systems has an ammonium picrate propellant which was developed to replace the Naval Propellant Laboratory's N-5 propellant presently used in Eagle-Picher gas generators. Due to the "N-5 replacement" intentions, burning rates and pressure-time characteristics should be comparable to that desired. Being machinable, the propellant provides the user versatility in configuration design. Additional properties include a high auto-ignition point and stability above 135°C.

The ammonium perchlorate propellants may be unstable when subjected to the extreme sterilization temperature in conjunction with the accompanying time lapse. Samples of this material offered by Talley Industries shall be tested.

3.0 CONCLUSIONS

No specific conclusions regarding testing to date have been made, pending completion of additional characteristic tests. It is evident that the polypropylene material, used in wet secondary sterilization applications, is not capable of surviving the dry sterilization routine. This would also apply to film type polypropylene and polyethylene materials.

Testing of electrolyte reservoirs or pyrotechnics has not been sufficient to justify any conclusions as yet.

4.0 RECOMMENDATIONS

Testing will continue to complete the characteristic study of absorbent type separation materials as well as Phase I requirements.

5.0 NEW TECHNOLOGY

No new technology was developed during the first quarter of the contract.